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Complexes Derived from Strong Field Ligands. XVIII. The Complexes of 2-(2-Mercaptoethyl)-pyridine with Nickel(II), Palladium(II), Platinum(II), and Cobalt(II)

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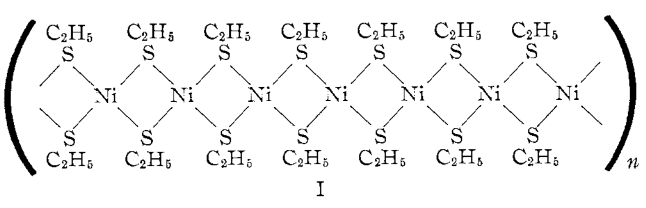
Received June 7, 1963

Three types of complexes of 2-(2-mercaptoethyl)-pyridine with divalent nickel, palladium, and platinum have been prepared and studied. Complexes of composition ML_2, where M is nickel, palladium, or platinum and L is the 2-(2-mercaptoethyl)-pyridino ion, were obtained in one isomeric form, probably of *cis* square-planar configuration. Complexes of composition $M_3L_4X_2$, where M is nickel or palladium and X is the perchlorate, nitrate, or methylsulfate ion, were prepared and found to be di-univalent electrolytes. A structure involving a complex cation in which two complexes of type ML_2 act as ligands toward a third metal ion is consistent with the properties of these compounds. A mixed metal complex of this structure containing two palladium atoms and one nickel atom has also been prepared. The third type of complex prepared with this ligand has the stoichiometry $M_2L_2X_2$, where M is nickel, palladium, or platinum and X is the chloride or bromide ion. These compounds are square-planar, sulfur-bridged complexes, probably of symmetrical configuration. Many other transition metal ions catalyze the oxidation of 2-(2-mercaptoethyl)-pyridine and make isolation of complexes difficult. However, a complex of the composition $Co_3L_4Cl_2 \cdot 2HCl$ has been prepared and, also, a mixed metal complex of composition $Ni_2CoL_4(ClO_4)_2$. In the case of Ni(II), the three complex species NiL_2, $Ni_2L_2X_2$, and $Ni_3L_4{}^{2+}$, may be interconverted under suitable conditions.

Introduction

The behavior of the mercaptide ion as a donor in transition metal complexes has not been subjected to such detailed study as is true of a number of other donor groups. This arises, in part, because the mercapto group often gives metal ion derivatives that are extremely insoluble, bridged, or even polymeric. Further, these substances commonly are easily oxidized. These properties greatly complicate the characterization of mercapto complexes; however, the theoretical interest and biological importance of mercaptans cause the elucidation of the manner of interaction of this function with metal ions to be of great interest.

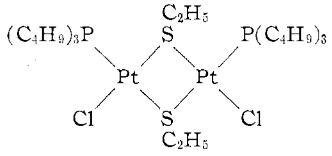
One of the more important properties associated with the mercaptide donor is its ability to form complexes containing sulfur bridges. The tendency of the group to form bridged complexes is illustrated by the nickel(II) complex of ethyl mercaptan, which has been found to be a diamagnetic, polymeric complex (structure I).[1]



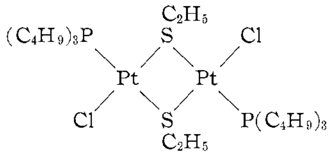
I

If other strong ligands are introduced, polymeric products can often be avoided, even under conditions favoring sulfur bridging. Thus, Chatt and Hart[2] prepared the *cis* and *trans* forms of dichlorobis-(tri-*n*-butylphosphine)-μ-ethylthiolodiplatinum(II) (structures II and III, respectively) and other similar complexes.

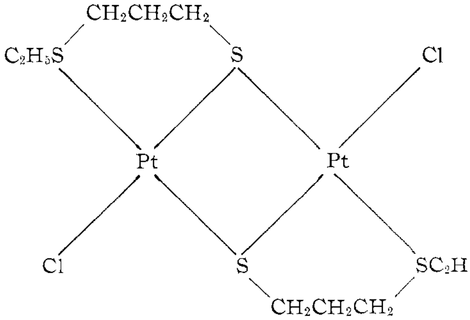
The same limited bridging can be caused by the use of bidentate ligands containing the mercapto group and another strong donor. Bridged complexes of platinum(II) and palladium(II) with ligands such as 3-ethylthiopropane-1-thiol have been prepared.[3,4] These are binuclear, sulfur-bridged complexes, as illustrated by the compound $Pt_2(C_2H_5SCH_2CH_2CH_2S)_2Cl_2$, which has been assigned structure IV.



II



III



IV

Other complexes of bidentate ligands containing the mercaptide group have recently been described by Jicha and Busch.[5-7] Derivatives of β-mercaptoethyl-

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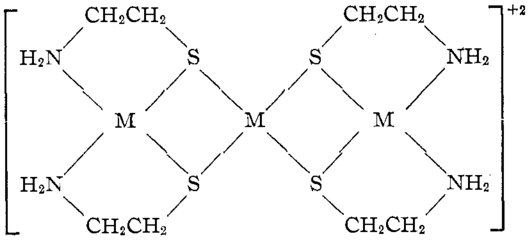
(1) K. A. Jensen, *Z. anorg. allgem. Chem.*, **252**, 227 (1944).
(2) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953).
(3) S. E. Livingstone, *ibid.*, 437 (1956).
(4) S. E. Livingstone, *ibid.*, 1989 (1956).
(5) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).
(6) D. C. Jicha and D. H. Busch, *ibid.*, **1**, 878 (1962).
(7) D. H. Busch and D. C. Jicha, *ibid.*, **1**, 884 (1962).

amine with several transition metal ions were reported. Well defined, monomeric compounds such as NiL_2 and PdL_2, where L = $NH_2CH_2CH_2S^-$, were isolated,[5] and it was found that these complexes react with divalent metal ions to form sulfur-bridged cations of structure V.[5,6]



V

The complex $Co(NH_2CH_2CH_2S)_3$ was also synthesized and found to combine with nickel(II) and cobalt(III) to give compounds containing the cations $[Ni(CoL_3)_2]^{+2}$ and $[Co(CoL_3)_2]^{+3}$, respectively.[7] It can be seen, then, that the tendency of the coordinated mercapto group to form sulfur-bridged compounds is great and that several different types of complexes containing mercaptide–sulfur bridges are known.

In order to investigate the characteristics of the mercaptide complexes further, particularly the bridging and reactivity of coordinated sulfur atoms, the present work was undertaken. The ligand studied, 2-(2-mercaptoethyl)-pyridine, is similar to β-mercaptoethylamine in its donor atoms but differs in stereochemistry and type of nitrogen atom and in the size of the chelate rings it may form.

Experimental

Magnetic Measurements.—Magnetic moments were obtained by the Gouy method using a field strength of approximately 8000 gauss. Iron(II) ammonium sulfate 6-hydrate and mercury(II) tetrathiocyanatocobaltate(II) were used as standards for the solid samples and nickel(II) chloride solution was used as standard for the liquid sample. Pascal's constants[8] were used to calculate the diamagnetism of the anions and water.

Conductivity Measurements.—Molar conductances were obtained from resistance measurements made with a Model RC 16 conductivity bridge manufactured by Industrial Instruments, Inc. A cell was used having a constant of 1.95, as determined by calibration with a solution of KCl of known concentration. All measurements were made in water or methanol at 25° at a concentration of close to 10^{-3} *M*.

Infrared Absorption Spectra.—A Perkin-Elmer Model 21 infrared recording spectrophotometer with sodium chloride optics was used to obtain all infrared spectra. The solid samples were prepared as potassium bromide pellets while sodium chloride capillary cells were employed for the liquid samples. Corrections were made for band frequencies using standard polystyrene spectra.

Molecular Weight Measurements.—Molecular weight measurements were made with a Model 301A vapor pressure osmometer manufactured by Mechrolab, Inc. Chloroform was used as the solvent and the instrument was calibrated with solutions of benzil of known concentration. Concentrations between 10^{-3} and 10^{-2} *M* were employed in the measurements.

Analyses.—All of the carbon, hydrogen, sulfur, and halogen and some of the nitrogen and metal analyses were performed by Galbraith Microanalytical Laboratories and Schwarzkopf Microanalytical Laboratories. Most of the nitrogen analyses were performed in this laboratory, using a Coleman Model 29 nitrogen analyzer. Some of the nickel analyses were performed in these laboratories using the dimethylglyoxime method as described by Mahin.[9]

2-[2-(Acetylthio)-ethyl]-pyridine.—This compound was prepared by the method of Vinton.[10] It was obtained as a colorless liquid, boiling point 139–140° (10 mm.). *Anal.* Calcd. for $C_9H_{11}NOS$: C, 59.6; H, 6.1; N, 7.7; S, 17.3. Found: C, 60.3; H, 6.6; N, 7.7; S, 17.3.

2-(2-Mercaptoethyl)-pyridine.—This compound was prepared by the method of Vinton.[10] It was obtained as a colorless liquid, boiling point 127–129° (40 mm.). *Anal.* Calcd. for C_7H_9NS: C, 60.4; H, 6.5; N, 10.1; S, 23.0. Found: C, 60.3; H, 6.8; N, 10.4; S, 22.8.

Bis-[2-(2-mercaptoethyl)-pyridino]-nickel(II).—$NiSO_4 \cdot 6H_2O$ (30 g., 1.14×10^{-1} mole) was dissolved in 200 ml. of concentrated NH_4OH (3.12 moles of NH_3) and 700 ml. of water. To this solution was added, with stirring, 10.5 g. (8.26×10^{-2} mole) of 2-(2-mercaptoethyl)-pyridine dissolved in 50 ml. of methanol. A dark brown oil separated from solution. After stirring overnight, the oil had solidified. The solid was separated by filtration and dried *in vacuo* over H_2SO_4 for 24 hr. The product was ground, washed with water, methanol, and ether, and dried again *in vacuo* over H_2SO_4; yield 6.5 g. (47%). *Anal.* Calcd. for $C_{14}H_{16}N_2NiS_2$: C, 50.2; H, 4.8; N, 8.4; S, 19.1. Found: C, 49.9; H, 4.7; N, 8.6; S, 19.0.

Dichlorobis-[2-(2-μ-mercaptoethyl)-pyridino]-dinickel(II). Method I.—$NiCl_2 \cdot 6H_2O$ (2.38 g., 1.0×10^{-2} mole) was dissolved in 100 ml. of absolute ethanol. To this solution was added slowly, with stirring, 1.39 g. (1.0×10^{-2} mole) of 2-(2-mercaptoethyl)-pyridine in 25 ml. of absolute ethanol. A black precipitate formed which was filtered, washed with absolute ethanol and ether, and then dried *in vacuo* over H_2SO_4; yield 1.2. g. (52%). *Anal.* Calcd. for $C_{14}H_{16}Cl_2N_2Ni_2S_2$: C, 36.2; H, 3.5; N, 6.0; Cl, 15.3. Found: C, 36.2; H, 3.5; N, 6.2; Cl, 15.2.

Method II.—$NiCl_2 \cdot 6H_2O$ (2.38 g., 1×10^{-2} mole) was dissolved in 100 ml. of absolute ethanol. To this solution was added 1.82 g. (1.0×10^{-2} mole) of 2-[2-(acetylthio)-ethyl]-pyridine in 25 ml. of absolute ethanol. No color change occurred, nor did a precipitate form upon the addition. The mixture was boiled on a steam bath for 20 min., whereupon the solution became dark and a black crystalline precipitate formed. The mixture was cooled, then filtered, and the black crystals were washed with absolute ethanol and ether and dried *in vacuo* over H_2SO_4; yield 0.5 g. (22%). *Anal.* Calcd. for $C_{14}H_{16}Cl_2N_2Ni_2S_2$: C, 36.2; H, 3.5; N, 6.0; S, 13.8; Cl, 15.3; Ni, 25.3. Found: C, 36.4; H, 3.5; N, 6.0; S, 13.7; Cl, 15.1; Ni, 25.1.

Tetrakis-[2-(2-mercaptoethyl)-pyridino]-trinickel(II) Perchlorate.—$Ni(ClO_4)_2 \cdot 6H_2O$(12 g., 3.27×10^{-2} mole) was dissolved in 50 ml. of methanol. To this solution was added slowly, with stirring, 4.4 g. (3.16×10^{-2} mole) of 2-(2-mercaptoethyl)-pyridine dissolved in 10 ml. of methanol. An orange precipitate formed which was filtered, washed thoroughly with methanol, and dried *in vacuo* over H_2SO_4; yield 2.65 g. (36%). *Anal.* Calcd. for $C_{28}H_{32}Cl_2N_4Ni_3O_8S_4$: C, 36.2; H, 3.5; N, 6.0; S, 13.8; Cl, 7.6. Found: C, 36.3; H, 3.6; N, 5.9; S, 13.7; Cl, 7.4.

Tetrakis-[2-(2-mercaptoethyl)-pyridino]-trinickel(II) Nitrate Dihydrate.—$Ni(NO_3)_2 \cdot 6H_2O$ (2.91 g., 1.0×10^{-2} mole) was dissolved in 100 ml. of absolute ethanol. To this solution was added slowly, with stirring, 1.39 g. (1.0×10^{-2} mole) of 2-(2-mercaptoethyl)-pyridine in 15 ml. of ethanol. A dark brown solution resulted. After a few minutes a red-brown precipitate began to form. The mixture was cooled, filtered, and the brown product washed with ethanol and ether and dried *in vacuo* over H_2SO_4; yield 1.1 g. (50%). *Anal.* Calcd. for $C_{28}H_{32}N_6Ni_3O_8S_4$: C, 37.8; H, 4.0; N, 9.4; Ni, 19.8. Found: C, 37.8; H, 4.4; N, 9.8, 9.5; Ni, 20.4.

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(8) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 26.

(9) E. G. Mahin, "Quantitative Analysis," 4th Ed., McGraw-Hill Book Co., New York, N. Y., 1932.

(10) W. H. Vinton, U. S. Patent 2,607,776 (1952).

Bis-[2-(2-mercaptoethyl)-pyridino]-palladium(II).—KCl (2.5 g., 3.35×10^{-2} mole) and 2.5 g. (1.4×10^{-2} mole) of $PdCl_2$ were dissolved in 250 ml. of water and 50 ml. of concentrated NH_4OH. To this solution was added, with stirring, 3.91 g. (2.8×10^{-2} mole) of 2-(2-mercaptoethyl)-pyridine dissolved in 10 ml. of water and 60 drops of concentrated HCl. A yellow precipitate formed immediately. Stirring was continued for 10 min., then the solution was filtered and the yellow solid washed with water, methanol, and ether and dried *in vacuo* over H_2SO_4; yield 3.9 g. (72%). *Anal.* Calcd. for $C_{14}H_{16}N_2PdS_2$: C, 43.9; H, 4.2; N, 7.3; S, 16.7. Found: C, 43.8; H, 4.4; N, 7.3: S, 16.6.

Dichlorobis-[2-(2-μ-mercaptoethyl)-pyridino]-dipalladium(II).—A 500-ml. sample of an aqueous solution containing 2.5 g. (3.35×10^{-2} mole) of KCl and 2.5 g. (1.4×10^{-2} mole) of $PdCl_2$ was mixed with a solution of 4.0 g. (2.87×10^{-2} mole) of 2-(2-mercaptoethyl)-pyridine in 30 ml. of absolute ethanol. A clear orange solution was produced. This solution was evaporated to about 100 ml. over steam and 500 ml. of absolute ethanol was added. The solution was again evaporated to about 100 ml. over steam, whereupon bright orange crystals precipitated. These were filtered, washed with water (to remove KCl, which coprecipitates), ethanol, and ether, and dried *in vacuo* over H_2SO_4; yield 0.8 g. (10%). *Anal.* Calcd. for $C_{14}H_{16}Cl_2N_2Pd_2S_2$: C, 30.0; H, 2.9; N, 5.0; Cl, 12.6. Found: C, 29.8; H, 3.1; N, 5.2; Cl, 12.6.

Bis-[2-(2-mercaptoethyl)-pyridino]-platinum(II) Monohydrate.—$PtCl_2$ (1.91 g., 7.2×10^{-3} mole) was dissolved in 50 ml. of concentrated NH_4OH and 100 ml. of water. To this solution was added 2.0 g. (1.44×10^{-2} mole) of 2-(2-mercaptoethyl)-pyridine in 25 ml. of methanol. Upon stirring and warming, a light orange oil began to collect around the bottom of the container. Stirring was continued overnight, during which time the oil solidified. The liquid was then decanted and the solid ground under methanol, filtered, washed with water, methanol, and ether, and dried *in vacuo* over H_2SO_4. The aqueous and methanolic filtrates were warmed, whereupon more solid precipitated. This solid was filtered, washed with water, methanol, and ether, and dried *in vacuo* over H_2SO_4; total yield 1.1 g. (31%). *Anal.* Calcd. for $C_{14}H_{18}N_2OPtS_2$: C, 34.3; H, 3.7; N, 5.7; S, 13.1. Found: C, 34.1; H, 3.4; N, 5.5, 5.6; S, 13.4.

Dichlorobis-[2-(2-μ-mercaptoethyl)-pyridino]-diplatinum(II).—$PtCl_2$ (1 g., 3.75×10^{-3} mole) and 1.0 g. (1.34×10^{-2} mole) of KCl were dissolved in 50 ml. of water. To this solution was added, with stirring, 0.6 g. (4.3×10^{-3} mole) of 2-(2-mercaptoethyl)-pyridine dissolved in 25 ml. of ethanol. A yellow precipitate formed at once. The mixture was warmed, with stirring, for 1 hr. and then filtered. The yellow solid was washed with water, ethanol, and ether and dried *in vacuo* over H_2SO_4; yield 1.15 g. (83%). *Anal.* Calcd. for $C_{14}H_{16}Cl_2N_2Pt_2S_2$: N, 3.8. Found: N, 3.6.

The above product is slightly soluble in chloroform, from which a small amount was recrystallized, giving canary yellow crystals. *Anal.* Calcd. for $C_{14}H_{16}Cl_2N_2Pt_2S_2$: C, 22.8; H, 2.2; N, 3.8; Cl, 9.6. Found: C, 23.1; H, 2.6; N, 3.4, 3.8; Cl, 9.4.

Tetrakis-[2-(2-mercaptoethyl)-pyridino]-tricobalt(II) Chloride Dihydrochloride.—$CoCl_2 \cdot 6H_2O$ (8.0 g., 3.36×10^{-2} mole) was dissolved in 100 ml. of methanol. To this solution was added slowly, with stirring, 4.0 g. (2.87×10^{-2} mole) of 2-(2-mercaptoethyl)-pyridine dissolved in 25 ml. of methanol. A dark green precipitate formed immediately. The solution and precipitate were cooled overnight. The mixture was filtered, giving a brown solid which was washed with small portions of methanol and dried *in vacuo* over P_2O_5; yield 1.8 g. (29%). *Anal.* Calcd. for $C_{28}H_{34}Cl_4Co_3N_4S_4$: C, 38.5; H, 3.9; N, 6.4; S, 14.7; Cl, 16.2; Co, 20.2. Found: C, 38.2; H, 3.9; N, 5.8, 6.4; S, 14.4; Cl, 16.4; Co, 20.6.

Reaction of Bis-[2-(2-mercaptoethyl)-pyridino]-nickel(II) with Nickel(II) Chloride. Preparation of Dichlorobis-[2-(2-μ-mercaptoethyl)-pyridino]-dinickel(II).—An excess of 0.5 *M* $NiCl_2 \cdot 6H_2O$ solution in methanol was added to a small amount of $Ni(C_5H_4NCH_2CH_2S)_2$ and the mixture was stirred for several minutes. The color of the solid changed from brown to red. The product was collected by filtration, washed with methanol and ether, and dried *in vacuo* over H_2SO_4. *Anal.* Calcd. for $C_{14}H_{16}Cl_2N_2Ni_2S_2$: N, 6.0. Found: N, 6.2.

Reaction of Bis-[2-(2-mercaptoethyl)-pyridino]-nickel(II) with Nickel(II) Perchlorate. Preparation of Tetrakis-[2-(2-mercaptoethyl)-pyridino]-trinickel(II) Perchlorate.—$Ni(C_5H_4NCH_2CH_2S)_2$ (1 g., 2.98×10^{-3} mole) and 2.0 g. (5.47×10^{-3} mole) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 100 ml. of methanol were stirred together for several minutes. The color of the solid changed from brown to orange during this time. Stirring, with slight warming, was continued overnight. The orange solid was collected by filtration, washed with methanol and ether, and dried *in vacuo* over H_2SO_4; yield 1.3 g. (94%). *Anal.* Calcd. for $C_{28}H_{32}Cl_2N_4Ni_3O_8S_4$: N, 6.0. Found: N, 5.7.

Reaction of Dichlorobis-[2-(2-μ-mercaptoethyl)-pyridino]-nickel(II) with Sodium Perchlorate. Preparation of Tetrakis-[2-(2-mercaptoethyl)-pyridino]-trinickel(II) Perchlorate.—A small amount of $Ni_2(C_5H_4NCH_2CH_2S)_2Cl_2$ was stirred with an excess of $Ni(ClO_4)_2 \cdot 6H_2O$ in methanol. After 1 hr. the color of the solid changed from red to orange. The product was filtered, washed with methanol and ether, and dried *in vacuo* over H_2SO_4. *Anal.* Calcd. for $C_{23}H_{32}Cl_2N_4Ni_3O_8S_4$: N, 6.0. Found: N, 5.6.

Reaction of Dichlorobis-[2-μ-mercaptoethyl)-pyridino]-nickel(II) with Sodium Perchlorate. Preparation of Tetrakis-[2-(2-mercaptoethyl)-pyridino]-trinickel(II) Perchlorate.—A small amount of $Ni_2(C_5H_4NCH_2CH_2S)_2Cl_2$ was stirred with an excess of $NaClO_4 \cdot H_2O$ solution in methanol. The mixture was refluxed for a few minutes, whereupon the color of the solid changed from red to orange. The product was filtered, washed with methanol and ether, and dried *in vacuo* over H_2SO_4. *Anal.* Calcd. for $C_{28}H_{32}Cl_2N_4Ni_3O_8S_4$: N, 6.0. Found: N, 5.9.

Reaction of Tetrakis-[2-(2-mercaptoethyl)-pyridino]-trinickel(II) Perchlorate with Nickel Chloride. Preparation of Dichlorobis-[2-(2-μ-mercaptoethyl)-pyridino]-nickel(II).—A small amount of $[Ni_3(C_5H_4NCH_2CH_2S)_4](ClO_4)_2$ was mixed with an excess of $NiCl_2 \cdot 6H_2O$ solution in methanol. In a short time the color of the solid changed from orange to red. The product was collected by filtration and washed with methanol and ether. To assure completion of the reaction, the product was ground and mixed again with excess $NiCl_2 \cdot 6H_2O$ solution in methanol. The product was again collected by filtration, washed with methanol and ether, and dried *in vacuo* over H_2SO_4. *Anal.* Calcd. for $C_{14}H_{16}Cl_2N_2Ni_2S_2$: N, 6.0. Found: N, 6.1.

Reaction of Bis-[2-(2-mercaptoethyl)-pyridino]-palladium(II) with Nickel(II) Nitrate, Followed by Addition of Sodium Perchlorate. Preparation of Tetrakis-[2-(2-mercaptoethyl)-pyridino]-dipalladium(II) nickel(II) Perchlorate.—One gram (2.61×10^{-3} mole) of $Pd(C_5H_4NCH_2CH_2S)_2$ was dissolved in an excess of $Ni(NO_3)_2 \cdot 6H_2O$ solution in methanol. An excess of $NaClO_4 \cdot H_2O$ solution in methanol was added, giving a red precipitate. The product was collected by filtration, washed with water, methanol, and ether, and dried *in vacuo* over H_2SO_4; yield 1.2 g. (90%). *Anal.* Calcd. for $C_{28}H_{32}Cl_2N_4NiO_8Pd_2S_4$: N, 5.5; Ni, 5.7; Pd, 20.8. Found: N, 5.3; Ni, 5.9; Pd, 20.3.

Reaction of Dichlorobis-[2-μ-(2-mercaptoethyl)-pyridino]-dinickel(II) with Ammonium Hydroxide. Preparation of Bis-[2-(2-mercaptoethyl)-pyridino]-nickel(II).—One gram (2.1×10^{-3} mole) of $Ni_2(C_5H_4NCH_2CH_2S)_2Cl_2$ was mixed with a solution of 15 ml. of concentrated NH_4OH and 85 ml. of water. After 5 min. the mixture was filtered, giving a pink filtrate. The filtrate was extracted with chloroform, giving a brown chloroform solution which was dried over Na_2SO_4. After filtering to remove the Na_2SO_4, the solution was evaporated *in vacuo* to a sirup and ether was added. Upon standing for several hours a small amount of brown solid had formed which was filtered, washed with ether, and dried *in vacuo* over H_2SO_4. *Anal.* Calcd. for $C_{14}H_{16}N_2NiS_2$: N, 8.4. Found: N, 8.4.

Reaction of Tetrakis-[2-(2-mercaptoethyl)-pyridino]-trinickel(II) Perchlorate with Ammonium Hydroxide. Preparation of Bis-[2-(2-mercaptoethyl)-pyridino]-nickel(II).—One gram (1.0×10^{-3} mole) of $[Ni_3(C_5H_4NCH_2CH_2S)_4](ClO_4)_2$ was added to a mix-

TABLE I

INFRARED BANDS AND ASSIGNMENTS (CM.$^{-1}$)[a,b]

Assignment	HL	NiL_2	PdL_2	PtL_2	$Ni_2L_2Cl_2$	$Pd_2L_2Cl_2$	$Pt_2L_2Cl_2$	$Ni_3L_4(NO_3)_2 \cdot 2H_2O$	$Ni_3L_4(ClO_4)_2$
py band I	1592 s	1595 s	1599 s	1598 s	1607 s	1613 s	1604 s	1614 s	1611 s
py band II	1569 s	1568 s	1574 s	1575 m	1577 w	1575 w	1563 w	1572 w	1568 w
py band III	1477 s	1473 s	1477 s	1478 s	1481 s	1488 s	1476 s	1487 s	1486 s
py band IV	1436 s	1431 s	1438 s	1438 s	1442 s	1452 s	1442 s	1446 s	1444 s
CH_2, wag	1307 w	1304 w	1306 w	1307 w	1315 m	1313 m	1306 m	1310 w	1309 w
	1278 m	1260 w	1264 w	1264 w	1260 s	1272 s	1261 s	1264 w	1262 w
C–H, d	752 s	774 s	772 s	772 s	774 sh	777 sh	772 sh	774 s	776 s
		749 s	750 s	750 s	764 s	770 s	760 s		
					753 sh				
NO_3^-								1384 s	
ClO_4^-									1085 s

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; d, deformation. [b] L = 2-(2-mercaptoethyl)-pyridino ion.

ture of 50 ml. of water and 50 ml. of chloroform. To the mixture was added 12 ml. of concentrated NH_4OH, with stirring. The chloroform phase became dark brown; the aqueous phase became pink. The brown chloroform phase was separated, dried over Na_2SO_4, and, after filtration, evaporated to a small volume. Ether was added and the mixture was allowed to stand for several hours. A dark solid formed which was filtered, washed with ether, and dried *in vacuo* over H_2SO_4. *Anal.* Calcd. for $C_{14}H_{16}N_2NiS_2$: N, 8.4. Found N, 8.0.

Reaction of Bis-[2-(2-mercaptoethyl)-pyridino]-nickel(II) with Cobalt(II) Perchlorate. Preparation of Tetrakis-[2-(2-mercaptoethyl)-pyridino]-dinickel(II)cobalt(II) Perchlorate.—One gram (2.98×10^{-3} mole) of $Ni(C_5H_4NCH_2CH_2S)_2$ was mixed with an excess of $Co(ClO_4)_2 \cdot 6H_2O$ dissolved in methanol. The solid changed in color from dark brown to red-brown. The mixture was filtered, and the solid was washed with methanol and ether and dried *in vacuo* over H_2SO_4; yield 1.0 g. (72%). *Anal.* Calcd. for $C_{28}H_{32}Cl_2CoN_4Ni_2O_8S_4$: N, 6.0; Ni, 12.7. Found: N, 5.9, 5.7; Ni, 12.7, 13.5, 12.9.

Discussion

Complexes of Nickel(II), Palladium(II), and Platinum(II).—The ligand, 2-(2-mercaptoethyl)-pyridine, reacts with nickel(II), palladium(II), and platinum(II) salts under various conditions to form three different types of complexes. In strongly ammoniacal solutions, complexes of the stoichiometry ML_2, where M is Ni, Pd, or Pt and L is the 2-(2-mercaptoethyl)-pyridino anion, are formed. In neutral solution, with metal salts of "noncoordinating" anions such as nitrate and perchlorate, complexes of the composition $M_3L_4X_2$, where X is the univalent anion, are obtained. In neutral solutions, with metal chlorides, complexes of the stoichiometry $M_2L_2Cl_2$ are formed. These complexes are easily differentiated by analysis and by their infrared spectra. The pertinent absorption bands in the infrared spectra of the three types of complexes are reported in Table I.

Complexes of the composition ML_2 have been synthesized with all three metals of the nickel group. This is particularly significant since Jicha and Busch[5] were unable to prepare a platinum compound of this type with β-mercaptoethylamine. The nickel complex is dark brown in color; the palladium complex, bright yellow, and the platinum complex, pale yellow. These compounds are diamagnetic (Table II), indicating that they have square-planar structures. Their solubilities are quite low in both polar and nonpolar solvents, but by heating or prolonged shaking they can be dissolved to a small extent in methanol and chloroform. The conductivity of the nickel complex in methanol indicates that it is a nonelectrolyte, having a molar conductance of 6 ohm^{-1} at 25° for a 1.22×10^{-3} *M* solution (Table III). The conductivity increases slightly with time, probably as a result of decomposition of the complex due to air oxidation of the ligand. The low solubilities of the complexes limited the accuracy of molecular weight measurements. This was further complicated by the apparent slow reaction of the complexes with air. Molecular weight data (Table IV) in chloroform

TABLE II

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF COMPOUNDS[a]

Compound	$\chi_M \times 10^{-6}$	T, °K.	μ_{eff}
HL	−88	303	. . .
NiL_2	−133	299	. . .
$Ni_2L_2Cl_2$	−151	299	. . .
$Ni_3L_4(ClO_4)_2$	−177	302	. . .
$Ni_3L_4(NO_3)_2 \cdot 2H_2O$	−110	302	. . .
PdL_2	−165	298	. . .
$CoNi_2L_4(ClO_4)_2$	4,046	299	3.12[b]
$Co_3L_4Cl_2 \cdot 2HCl$	14,566	299	3.42

[a] L = 2-(2-mercaptoethyl)-pyridino ion. [b] All of the paramagnetism attributed to Co.

TABLE III

MOLAR CONDUCTANCES OF THE COMPLEXES[a]

Compound	Solvent	Concn., *M*	ΛM, ohm^{-1}
NiL_2	CH_3OH	1.22×10^{-3}	6
$Ni_2L_2Cl_2$	CH_3OH	1.31×10^{-3}	128
		7.5×10^{-4}	146
$Ni_3L_4(NO_3)_2$	H_2O	1.22×10^{-3}	227
$Ni_3L_4(CH_3SO_4)_2$[b]	H_2O	1.05×10^{-3}	186
		5.8×10^{-4}	201
$Co_3L_4Cl_2 \cdot 2HCl$	CH_3OH	1.30×10^{-3}	214

[a] L = 2-(2-mercaptoethyl)-pyridino ion. [b] Synthesis reported by D. C. Jicha, J. W. Wrathall, and D. H. Busch, in press.

TABLE IV

MOLECULAR WEIGHTS OF THE NEUTRAL COMPLEXES[a]

Compound	Molecular weight	
	Theory	Obsd.
NiL_2	335	274
PdL_2	383	324
$Ni_2L_2Cl_2$	465	404
$Pd_2L_2Cl_2$	561	528

[a] L = 2-(2-mercaptoethyl)-pyridino anion.

for the nickel and palladium complexes yielded values some 15–20% lower than theory for the monomer. Despite the stated difficulties, this indicates that the compounds are monomeric. These complexes are, therefore, square-planar, monomeric, nonelectrolytes. They can, theoretically, exist as *cis* or *trans* isomers or a mixture of both. In this investigation, no evidence for more than one form was obtained. The obvious method for determination of which isomer has been obtained, that of dipole moment measurement, was impossible due to solubility restrictions. As will be seen, however, the reactions of these compounds with metal salts indicate a *cis* configuration. This is consistent with the behavior of β-mercaptoethylamine.[5]

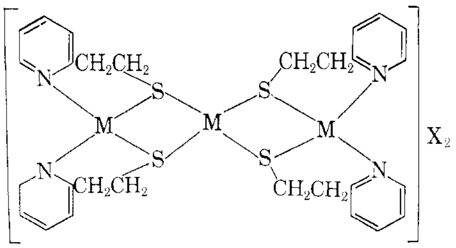
Nickel(II) nitrate and nickel(II) perchlorate react with 2-(2-mercaptoethyl)-pyridine in neutral methanolic solution to give complexes of the composition $Ni_3L_4X_2$, where X is NO_3^- or ClO_4^-. The perchlorate salt is quite insoluble in both polar and nonpolar solvents, whereas the nitrate salt is soluble in water and the lower alcohols. The molar conductance of $Ni_3L_4(NO_3)_2$ in water is 227 ohm^{-1} at 25° for a 1.22×10^{-3} *M* solution (Table III), indicating that it is a di-univalent electrolyte. The compounds are diamagnetic (Table II) and, therefore, involve square-planar coordination.

In addition to synthesis by direct reaction of the ligand with metal salts, these compounds can be prepared by an alternative method. For example, the reaction of NiL_2 with nickel(II) perchlorate gives $Ni_3L_4(ClO_4)_2$, according to the equation

$$2NiL_2 + Ni(ClO_4)_2 \rightleftharpoons Ni_3L_4(ClO_4)_2$$

The mixed metal complex $NiPd_2L_4(ClO_4)_2$ has been prepared in this way by reaction of PdL_2 with $Ni(NO_3)_2$ in methanol, followed by addition of $NaClO_4$.

All of the above characteristics of complexes of this type, *i.e.*, composition, conductivity, magnetic susceptibility, and capability of being synthesized by the reaction of metal salts with complexes of the type ML_2, indicate that they are bridged complexes of structure

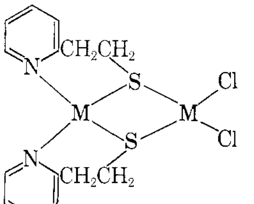


VII

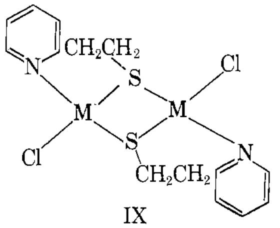
analogous to those proposed by Jicha and Busch[5,6] for β-mercaptoethylamine complexes. It is interesting that the anions in this type of complex must be "noncoordinating" anions such as nitrate and perchlorate. Attempts to prepare complexes with metal halides resulted in the isolation of compounds with a metal–ligand ratio of one to one. This was not the case when β-mercaptoethylamine was used as a ligand. In fact, most of the salts of $M_3(H_2NCH_2CH_2S)_4^{+2}$ prepared by Jicha and Busch involved halide anions.

Chloro complexes of the type $M_2L_2Cl_2$, where L is, again, the 2-(2-mercaptoethyl)-pyridino ion, have been prepared for all three of the nickel group metals. These compounds are obtained by direct reaction of the ligand with the corresponding metal salt in neutral solution. They are all crystalline in character; the nickel derivative is dark red-brown, the palladium compound orange, and the platinum complex yellow. The compounds are slightly soluble in chloroform and, to a lesser extent, in methanol. They are dimeric, as indicated by molecular weight data (Table IV). The values, measured in chloroform, are between 10 and 20% lower than theory. This is, as in the case of complexes of type ML_2, probably due to decomposition caused by air oxidation. The complexes are diamagnetic (Table II).

Several structures, involving either chloride or sulfur bridging, are possible for these compounds. However, alkylation reactions[11] indicate that both sulfur atoms in the complexes of the type $M_2L_2Cl_2$ are bridged. Therefore, either structure VIII or IX must be involved.



VIII



IX

Unfortunately, a definite assignment of one of these structures is not possible. Dipole moment measurements are, again, impossible because of solubility limitations. Attempted preparation of mixed metal complexes by the reactions

$$PdL_2 + NiCl_2 \longrightarrow$$
$$NiL_2 + K_2PdCl_4 \longrightarrow$$

which might have differentiated between the structures (the symmetrical structure would result in the same product in both reactions; the unsymmetrical structure would result in two different isomers) yielded products which had nonstoichiometric ratios of metal atoms. This result implies substantial equilibration and is most consistent with the symmetrical structure.

As has been noted, complexes of analogous composition have previously been prepared with other ligands. Livingstone[3,4] prepared several complexes of 3-ethylthiopropane-1-thiol and similar ligands. The symmetrical structure IV was assumed. No serious consideration was given to the possibility of an unsymmetrical structure, although most of the experimental observations did not distinguish between the two. It was found, however, that the oxalato complex of composition $Pd_2((CH_3)_2AsCH_2CH_2CH_2S)_2(C_2O_4)$ was much less soluble than similar complexes with monodentate anions and this was attributed to a polymeric

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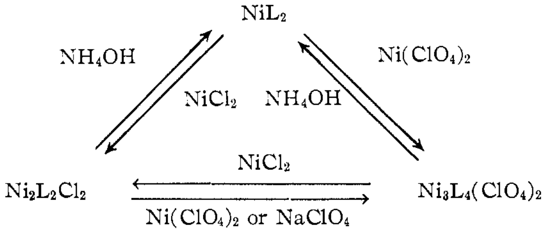
(11) D. C. Jicha, J. W. Wrathall, E. Blinn, and D. H. Busch, *J. Am. Chem. Soc.*, in press.

structure for the oxalato complex. A polymeric oxalato complex would indicate the symmetrical form for complexes of this type.

The three types of complexes which 2-(2-mercaptoethyl)-pyridine forms with divalent metal ions of the nickel group have all been observed with other ligands. However, no other ligand has been observed to form all three types. These results emphasize the importance of reaction conditions and type of anion on the structure of complexes and, also, show the versatility of the mercaptide donor in forming complexes of varying structure.

The different types of complexes are readily converted one to another under the proper conditions. Thus, with nickel as the metal, the reactions shown in Scheme I have been carried out. The products in these reactions (which are described in the Experimental section) were identified by infrared spectra and analysis.

SCHEME I



Complexes with Other Metals.—The attempted preparation of complexes of 2-(2-mercaptoethyl)-pyridine with metals other than those of the nickel group was unsuccessful, except in the case of cobalt. A product of stoichiometry $Co_3L_4Cl_2 \cdot 2HCl$ was obtained in the reaction of $CoCl_2$ with the ligand in methanol. The structure of this complex remains in question.

Mixed Metal Complexes.—In the investigations of Jicha and Busch[5,6] with complexes of β-mercaptoethylamine, a number of mixed metal derivatives containing complex ions of the type shown in structure V were prepared by reaction of bis complexes $M(NH_2CH_2CH_2S)_2$, with metal salts. In this investigation also, attempts were made to prepare bridged derivatives containing more than one metal by reaction of the complexes ML_2 with metal salts. The results of the reaction of PdL_2 with Ni^{+2} have already been mentioned. In this case the mixed metal complex $NiPd_2L_4(ClO_4)_2$ was obtained.

The reactions of NiL_2 with several divalent metal salts of the first transition series were also investigated. Metal ions used were Mn^{+2}, Fe^{+2}, Co^{+2}, and Cu^{+2}. The only mixed metal complex obtained was $CoNi_2L_4(ClO_4)_2$, which was prepared by shaking the solid NiL_2 with a methanolic solution of $Co(ClO_4)_2$. The other metal ions appear to catalyze oxidation of the ligand and attempted isolation of stoichiometric products was unsuccessful.

The preparation of the mixed metal Co–Ni and Ni–Pd complexes in the manner described is a strong indication that complexes of the type ML_2 are *cis* in configuration. A *trans* configuration would require dissociation of the ligand from the metal during the course of the reaction and should lead to nonstoichiometric ratios of metals in the resulting bridged complexes.

Acknowledgment.—The financial support of the U. S. Army Medical Research and Development Command is gratefully acknowledged.

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Preparation and Reduction of Bis-(3-nitro-2,4-pentanediono)-beryllium

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Received February 21, 1963

Reaction of 2,4-pentanedione with beryllium nitrate trihydrate in acetic anhydride gave bis-(3-nitro-2,4-pentanediono)-beryllium (compound I). This was reduced catalytically to the corresponding amine (II). Bis-(2,4-pentanediono)-beryllium reacted in this nitrating medium to yield a polymeric nitrated complex containing hydroxo bridges (VI). This was converted to either the methoxo or ethoxo bridged complexes (VII and VIII) by boiling in methanol or ethanol. These were shown by molecular weight studies to be partially trimeric.

The nitration of chromium(III), cobalt(III), and rhodium(III) acetylacetonates has been reported by Collman and co-workers,[2] who used cupric nitrate trihydrate in acetic anhydride as the nitrating agent. Their attempts to reduce these to the corresponding amino-substituted complexes, however, were unsuccessful.[3]

The amino type of complex is of interest because of the reactions which the functional group might undergo, particularly diazotization, which could be followed by the substitution of various other functional groups onto the chelate ring.

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[1] Abstracted from a portion of the Ph. D. thesis of Richard M. Klein, 1963.

[2] J. P. Collman, R. L. Marshall, W. L. Young, III, and S. D. Goldby, *Inorg. Chem.*, **1**, 704 (1962).

[3] Since submission of this paper, it has been brought to our attention that more recent experiments have resulted in the reduction of the nitro-substituted chromium(III) acetylacetonate to the amino chelate. The latter substance forms a stable diazonium salt. J. P. Collman and M. Yomada, Southeastern Regional Meeting of the American Chemical Society, Gatlinberg, Tenn., Nov., 1962; *Chem. Ind.* (London), in press.